



Removal of Cd(II) ions from contaminated water by a new modified magnetic chitosan nano composite

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ARTICLE INFO

Article history:

Received 1 November 2018

Received in revised form

20 April 2019

Accepted 22 April 2019

Keywords:

Removal of Cd(II)

Magnetic chitosan nanocomposites

Additive

N- Nicotinyl phosphoric triamide Amine

ABSTRACT

Magnetic chitosan nanocomposites are one of the more recent advanced groups of adsorbents used to remove contaminants from waste water. In this research, N-Nicotinyl-N', N''-bis (Hexamethylenyl) phosphoric triamide (HE) was used as an additive to form a new nanocomposite with the structure of chitosan / 5% Fe₃O₄ Nps/10% HE resulting in the highly efficient removal of Cd(II) ions from an aqueous solution. Several techniques were applied to characterize the new-fabricated nanocomposite: X-ray Powder Diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Field Emission Scanning Electron Microscopy (FE-SEM), Fourier transform infrared (FTIR) and vibrating sample magnetometer (VSM). Atomic Absorption Spectroscopy (AAS) was used to measure the removal percentage of Cd(II) ions from the contaminated water samples. Results showed that 15 mg of the nanocomposite could remove Cd(II) ions with a rate of 99.9% from 20 mL of its 100 ppm aqueous solution in pH=9 with contact time of 1h. Furthermore, the same amount of the nanocomposite was applied to remove Cd(II) ions from 20 mL of a real wastewater sample with a pH=9 and the same contact time. The resulting removal rate of Cd(II) ions was 99.5%.

1. Introduction

Water is an essential human resource and has economic, political and environmental importance all over the world. Since heavy metal ions have toxic effects on human health, many studies have focused on removing these micropollutants [1-3]. Cadmium is one of the transition metals with many applications in different industries. The major sources of cadmium waste include batteries, metal refineries, smelting, mining, refining of nonferrous metals, Cd-plated steel scrap and pigments [6,7]. Cadmium has been listed as a carcinogen by the US Environmental Protection Agency (EPA) and the International Agency for Research on cancer [8]. Recently, there has been a great interest in using chitosan nanocomposite derivatives as a water treatment agent [9,10]. Separation methods that employ magnetic adsorbents are important techniques for treating wastewater and have received considerable attention in recent years [11-14]. The main benefit of magnetic separation is that a large amount of water can be

purified in a short period of time using less energy and without producing pollutants [15]. Magnetic chitosan composites containing a matrix of chitosan polymer and a dispersed phase including magnetic particles have grabbed great attention in environmental areas such as pollutant degradation, contaminant removal [20-23] and especially in water treatment [28-31]. Apart from the magnetic nanoparticles, many other compounds have been applied as additives in chitosan based nanocomposites. For example, 2-aminopyridine glyoxal Schiff's base has been added to chitosan/Fe₃O₄ magnetic nanocomposites to enhance the removal rate of Cd(II), Cu(II), and Ni(II) ions [32]. In this study, we embedded N- Nicotinyl-N', N''-bis (Hexamethylenyl) phosphoric triamide (HE) in the structure of a magnetic chitosan nanocomposite, as a new additive, to investigate its effect on the removal rate of Cd(II) ions. Phosphoric triamides are an important class of organophosphorus compounds with a wide range of applications in different fields. They have been studied as anticancer prodrugs, enzyme inhibitors, insecticides and

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DOI: 10.22104/aet.2019.3216.1159

pesticides, catalysts for different chemical reactions, and efficient ligands in coordination chemistry [33-42]. In our previous work [30], we studied the effect of chitosan/ 10% N- Nicotinyln-N', N''-bis (pyrrolidinyl) phosphoric triamide/ 5% Fe₃O₄ NPs on the removal rate of Cu (II). We found that by adding a 10% phosphoric triamide derivative to the structure of the magnetic chitosan nano composite, the removal of the Cu(II) ions clearly improved with an optimal removal of 89.44 % from the 100mg/L copper nitrate (II) aqueous solution in a pH=9. In this research, we prepared a new cross-linked magnetic nanocomposite: chitosan / 5% Fe₃O₄ Nps/10% N-Nicotinyln-N', N''-bis (Hexamethylenyl) phosphoric triamide (HE). It was characterized by several techniques including XRD, FE-SEM and EDX, FTIR and VSM. Then, the fabricated nano composite was used to remove Cd(II) ions from two kinds of contaminated water samples for which both had a pH=9 : aqueous solution sample and real wastewater sample from a factory. A pH=9 was chosen for two reasons: 1) The pH of the industrial wastewater sample was 9; and 2) In our previous work [30], the best result of copper (II) ions removal by a very similar nanocomposite had been obtained in a pH=9.

2. Materials and methods

The high molecular weight chitosan was purchased from Loba Chemie Pvt. Ltd. The ferric nitrate, ferrous chloride tetra hydrate, PCl₅, hexamethyleneimine, CCl₄, acetonitrile, acetic acid, starch and distilled water were obtained from the Merck Co. The nicotinamide was purchased from the Acros Co. The glutar aldehyde (25 wt% in water) was purchased from the Daejong Co. The industrial wastewater sample was obtained from the Narin metal plating factory located in Shahriar, Iran. The magnetic behavior of Fe₃O₄ NPs was investigated using a vibrating sample magnetometer (VSM), model: 7407, Lake Shore Co. The phase analysis of the fabricated framework was done by an X-ray Diffraction device, model: Equinox 3000, Intel Co. The morphology and elemental quantities of the nanocomposite were investigated by Field Emission Scanning Electron Microscopy, model: Mira II, Tescan Co. and Energy Dispersive Spectroscopy, model: Mira II, Tescan Co. instruments. An ultrasonic bath (model: S 4000, Misonix Co.) with an output power of 600W was used in the preparation process. The removal rate of Cd(II) ions by the prepared nanocomposite was determined by using atomic absorption spectroscopy (AAS), model: AAS-240-Varian Co.

2.1. Synthesis of N- Nicotinyln- N', N''-bis (hexamethylenyl) phosphoric triamide (HE)

The phosphoric triamide was synthesized using a published procedure [36]. Briefly, Hexamethyleneimine (4 mmol) was added to a mixture of N-Nicotinyln phosphoramidic dichloride (1 mmol) and Acetonitrile at 0 °C. After 8 h, the mixture was filtered; the remaining precipitate was dried at 25 °C after washing with distilled water [36].

2.2. Synthesis of Fe₃O₄ nanoparticles

The magnetite Fe₃O₄ NPs were synthesized by a general method reported in the literature [43]. A mixture of FeCl₂·4H₂O (1 mmol) and anhydrous Fe (NO₃)₃ (2 mmol) in ethanol plus 20 mmol of starch was stirred at the pH of 8 for 1 h at atmospheric pressure. Then the precipitate was purified by washing with ethanol and dried in a vacuum situation [43].

2.3. Fabrication of Chitosan/ Fe₃O₄ NPs/ HE nanocomposite

Acetic acid (3 mL) was added to a suspension containing 0.5 g of chitosan in 5 mL distilled water, and the mixture was put in an ultrasonic bath for 2 h to yield a homogenous gel. Then a mixture of 0.05 g (10 % weight of chitosan) HE with ethanol was poured into the gel and put in the ultrasonic bath for 30 min. Next, 0.025 g (5% weight of chitosan) of Fe₃O₄ NPs was added and put in an ultrasonic bath for 30 min again. After that, for the best dispersion of the NPs and phosphoric triamide compounds in the chitosan framework, an ultrasonic probe was applied to sonicate the mixture. The films produced from drying the mixture in the petri-dish were allowed to remain in desiccators containing glutar aldehyde steam with the pressure of 0.5 °atm for 24 hours to complete the cross-linking process of chitosan. Finally, these films were washed with ethyl alcohol, acetic acid and distilled water to remove the non-cross-linked chitosan and un-reacted residual glutar aldehyde; then, they were dried at room temperature.

2.4. Cd(II) ions removal with Chitosan/ Fe₃O₄ NPs/ HE nanocomposite

A Cd(II) ion solution of 20 mL with a concentration of 100 mg/l was prepared by diluting its commercial stock sample. The pH was set on 9 by using HNO₃ and NH₃, both with a concentration of 0.1 M. 15mg of the adsorbent (nanocomposite) was poured into the solution and shaken for 1h on a thermostatic shaker at 150 rpm at 25 °C. Then the solid phase was separated by a magnet.

3. Results and discussion

3.1. X-Ray diffraction (XRD) analysis

In order to confirm the structure of the nanocomposite, the XRD pattern of the nanocomposite was investigated and compared with the patterns of its components. Figures 1 – 4 show the XRD patterns of Fe₃O₄ NPs [44], chitosan and phosphoric triamide (HE) [45] in comparison to the XRD pattern of the new fabricated nanocomposite.

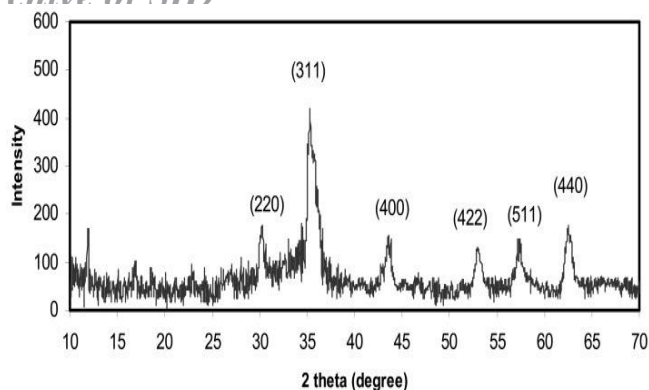


Fig.1. XRD pattern of Fe₃O₄ NPs [44].

The characteristic diffraction peaks of the Fe₃O₄ NPs in its XRD graph could be indexed as (220), (311), (400), (422) and (333) planes, based on the standard cards [44] (Figure1). As shown in Figures 1 and 2, all of these peaks are observable in the XRD pattern of the fabricated nanocomposite. The broad XRD pattern of Fe₃O₄ refers to its nano-sized structure. N- NicotinyI-N', N''-bis (Hexamethylenyl) phosphoric triamide (HE) has a pattern with sharp peaks, due to its high crystallinity [45] (Figure 3). As it can be observed in the XRD pattern of the fabricated nanocomposite (Figure 2), the intensity of the phosphoric triamide peaks changed because of the use of ultrasonic waves in the mixing process, while there is no obvious effect of the dispersant on the structures of the phosphoric triamide and Fe₃O₄ magnetic particles.

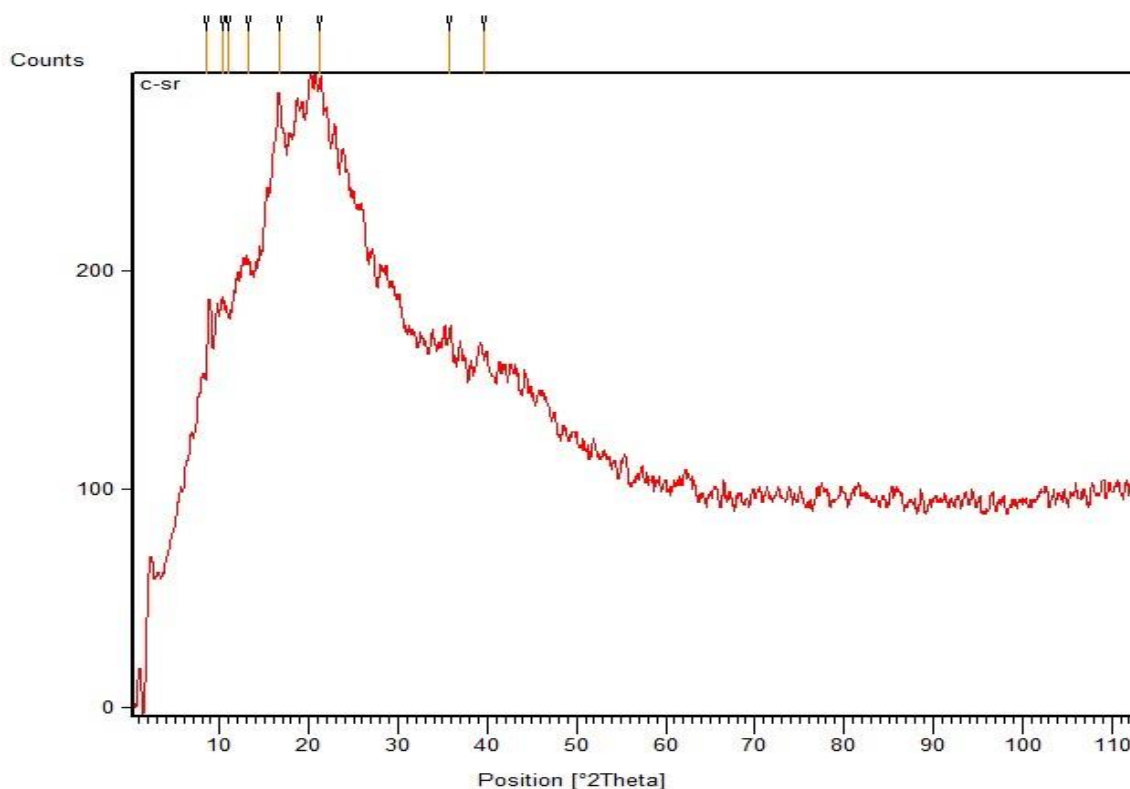


Fig. 2. XRD pattern of nanocomposite chitosan / 5% Fe₃O₄ Nps/10% HE.

Chitosan has broad XRD patterns, due to its polymeric amorphous structure, with an intense peak in $2\theta = 20^\circ$ (Figure 4). The XRD of the fabricated nanocomposite, chitosan / 5% Fe₃O₄ Nps/10% HE, showed a broad pattern (Figure 2); this could be owing to the use of ultrasonic waves in the mixing process and the amorphous phase of chitosan, which appears as a maximum scattered phase

on the background. As it can be seen in Figure 2, despite the broad XRD pattern of the nanocomposite, all the characteristic diffraction peaks of HE, chitosan and Fe₃O₄Nps are observable in the XRD graph of the nanocomposite, which confirms the unchanged phases of the components in the nanocomposite framework.

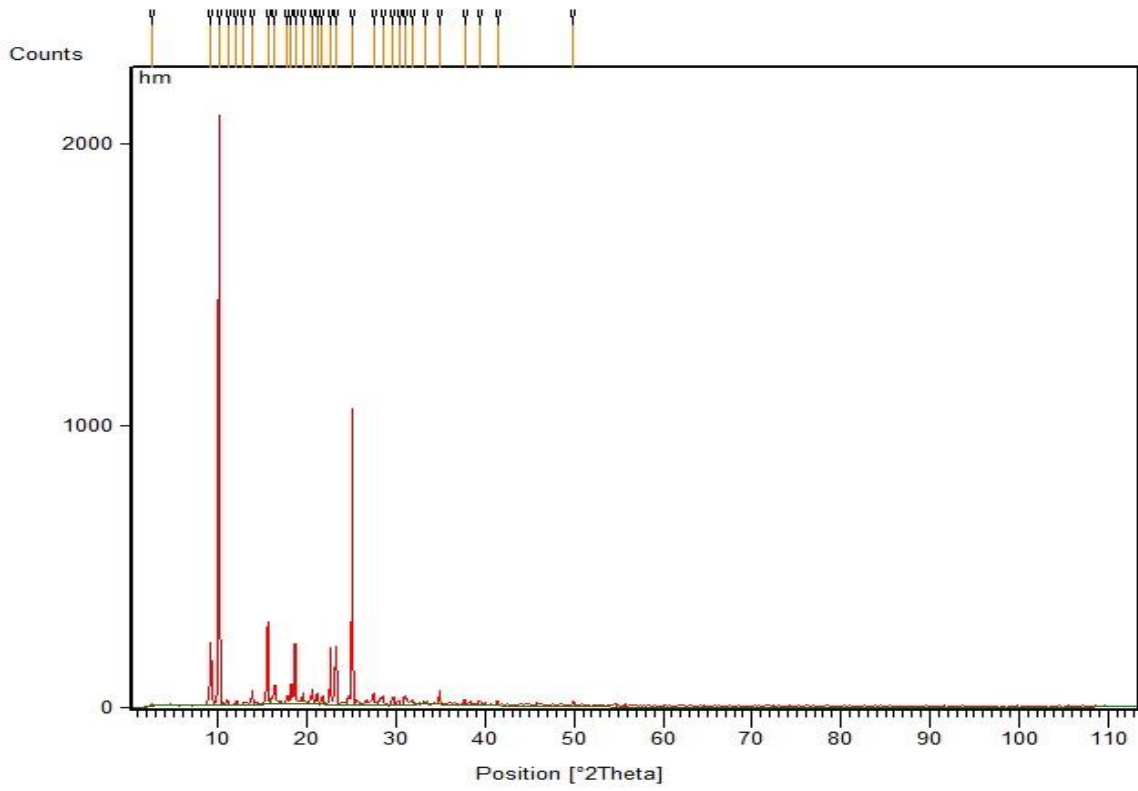


Fig.3. XRD pattern of HE [45].

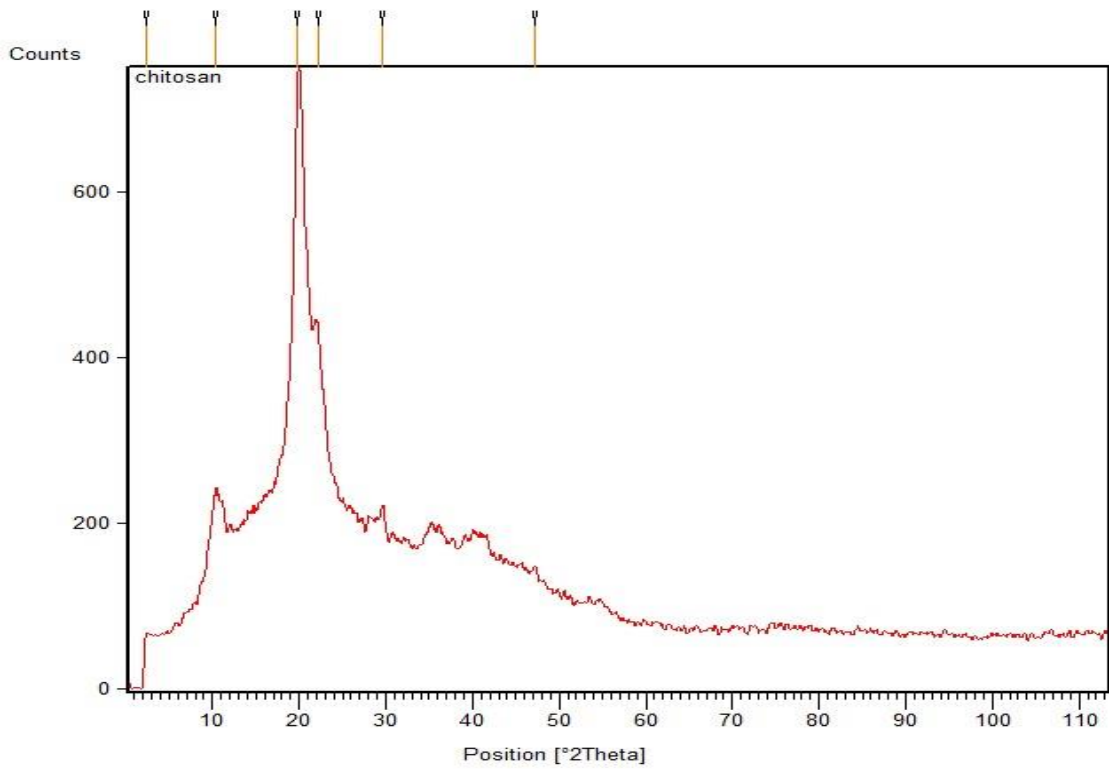


Fig.4. XRD pattern of chitosan.

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3.2. FE-SEM micrographs and EDX

Field Emission Scanning Electron Microscopy was used to investigate the surface morphology and estimate the average particle sizes (Figure 5). The SEM image of the Fe_3O_4 nanoparticles demonstrated their uniform spherical with

the diameter of, mostly, under 100 nm that confirmed the nano size of these particles (Figure 5a). The presence of % Fe_3O_4 NPs can be obviously observed in the construction of the fabricated nanocomposite (Figure 5b). Its good surface with a homogenous dispersion of the components could be due to the proper stirring time under ultrasonic waves.

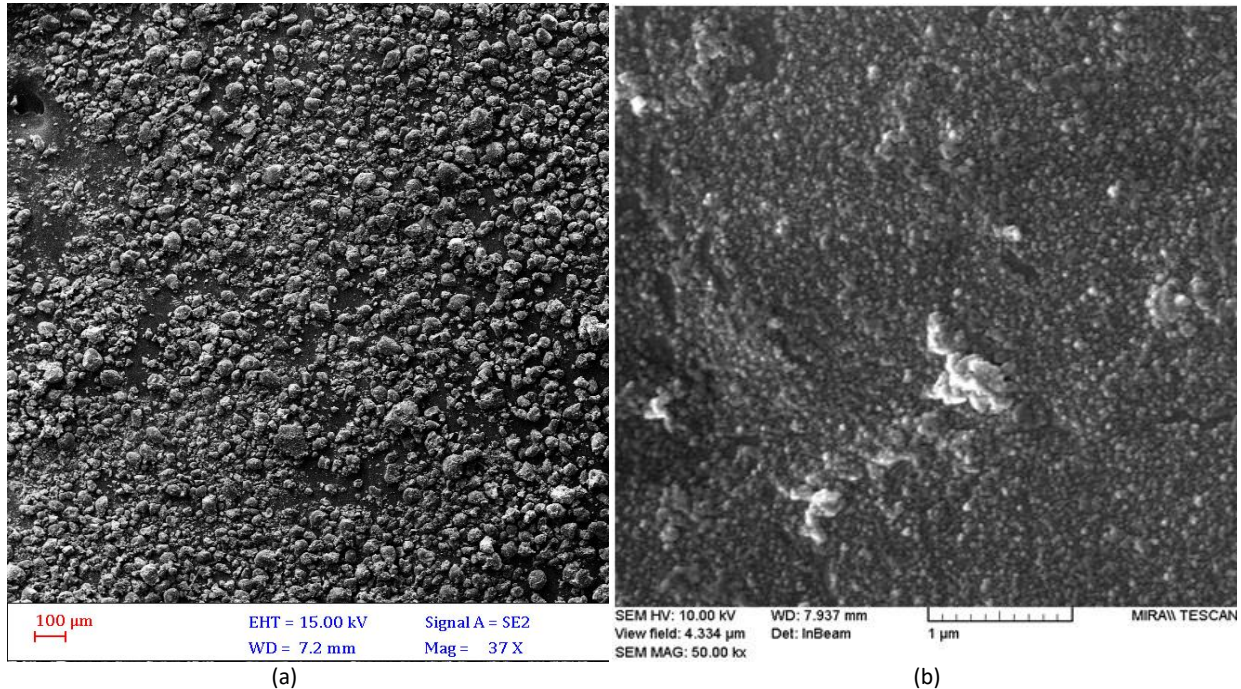


Fig. 5. FE-SEM micrograph of Fe_3O_4 nanoparticles (a) & nanocomposite chitosan / 5% Fe_3O_4 Nps/10% HE (b).

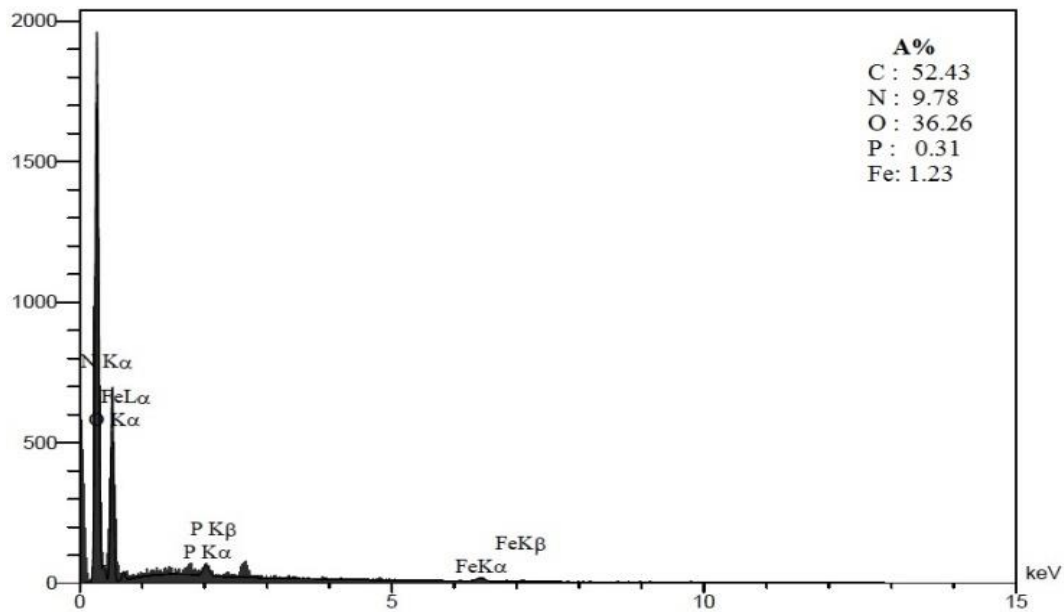


Fig. 6. EDS elemental analysis of nanocomposite chitosan / 5% Fe_3O_4 Nps/10% HE.

Energy Dispersive Spectroscopy was applied to prove the presence of all the initial components and all their elements in the nanocomposite framework. The EDS analysis of the prepared nanocomposite chitosan / 5% Fe_3O_4 Nps/10% HE

is exposed in Figure 6, which confirms the existence of all the designed parts within the nano film and validates the desired percentages of the elements.

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3.3. VSM analysis

The magnetic hysteresis loops of the Fe_3O_4 NPs and the fabricated nanocomposite are presented in Figure 7. As it is observable from the hysteresis loops, with respect to the saturation magnetization scale, the Fe_3O_4 NPs show a superparamagnetic behavior. It means that this magnetic nanocomposite adsorbent can be considered as an

economic water purifier that can be easily removed by a magnetic field after removing the metal ions. The measured saturation magnetization for Fe_3O_4 NPs and the nanocomposite were 63.37 and 29.94 emu/g, respectively. The lower magnetization value of the nanocomposite compared to the naked Fe_3O_4 NPs could be due to the coverage of the magnetic Fe_3O_4 NPs by the non-magnetic matrix of the other components.

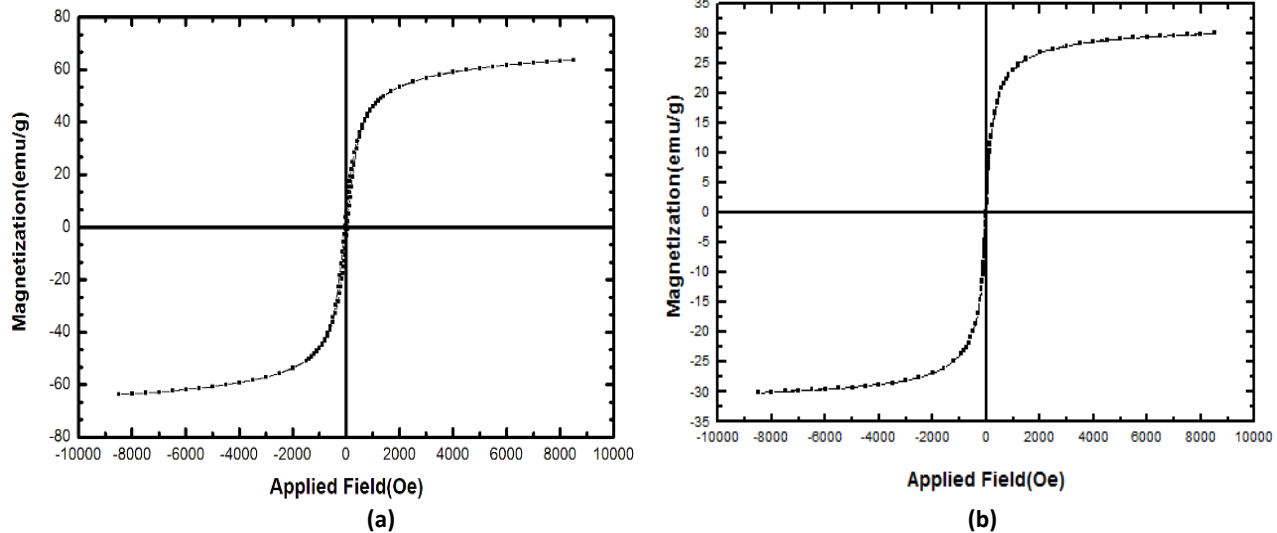


Fig.7. Magnetic hysteresis loops of Fe_3O_4 nanoparticles (a) and fabricated nanocomposite (b).

3.4. Removal of metal ions

Since our aim was to fabricate a nanocomposite for removing Cd(II) ions from the industrial wastewater of the Narin metal-plating factory at a high rate, we considered two points in this study:

1. We chose a pH=9 because the pH of the mentioned industrial wastewater was 9.
2. We formulated our nanocomposite with a very similar structure (both in percentage and type of components) to our previously reported nanocomposite [30], which was successful in the removal of Cu (II) ions in a pH=9.

In our previous work, we studied the structure effect of chitosan/N- Nicotinyln-N', N''-bis (pyrrolidiny) phosphoric triamide/ Fe_3O_4 NPs nanocomposite on the removal amount of Cu (II) ions. We found that the optimal removal of the Cu (II) ions was achievable when 10% of the phosphoric triamide was used in the nanocomposite structure as well as when we used this nanocomposite to remove the Cu(II) ions from its aqueous solution in a pH=9 [30]. So, here we devised a new nanocomposite containing chitosan, 10% of a new phosphoric triamide derivative (HE), and 5% of Fe_3O_4 NPs. The use of 15 mg of this nanocomposite to remove Cd (II) ions from 25 mL of its 100 mg/L aqueous solution in a pH=9 resulted in a 99.9% removal rate of the cadmium ions (Table 1).

Table 1. Maximum removal percentage of Cd(II) ions obtained by some nanocomposites.

Nanocomposite	Maximum Removal Percentage of Cd(II)	Ref.
chitosan / 5% Fe_3O_4 Nps/10% N- Nicotinyln-N', N''-bis (Hexamethylenyl) phosphoric triamide (HE)	99.9	Present work
EDTA-and/or DTPA-cross-linked chitosan	85.84	[46]
Cross-linked magnetic chitosan-2-aminopyridine glyoxal Schiff's base	70.7	[47]
α -ketoglutaric acid-modified magnetic chitosan	93	[48]

The removal rate was determined via AAS. The test and the measurement were repeated three times. Since the removal rate of the Cd(II) ions in the aqueous solution was high, the same amount of this nanocomposite, with the same contact time(1h), was used for removing the Cd(II) ions from 20 mL of the real wastewater sample of the Narin metal plating factory with a pH=9. The cadmium ions removed in this real sample was 99.5% and contained other unknown ions and materials. It appeared that there were some undesired interactions in the real sample. Due to the unknown complex structure of the factory's wastewater,

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the interactions were unidentified; therefore, we could only talk about the sufficiency of the removal ability of our nanocomposite. Comparing the Cd (II) removal percentage obtained by our fabricated nanocomposite with those obtained by some other structurally similar composites in aqueous solutions [46-48] confirmed the good ability of our devised nanocomposite in removing Cd(II) ions (Table 1). Table 1 shows that the ability of our devised nanocomposite in removing Cd(II) ions was higher than other similar nanocomposites in aqueous solution (99.5%). Although the efficiency of the nanocomposite in removing of Cd (II) ions decreased in the real industrial wastewater sample, its removal rate (99.5%) was still higher than those for other similar nanocomposites used in the desired situation of aqueous solutions [46-48].

4. Conclusions

Building on the results of our previous work, a new nanocomposite with the structure of chitosan / 5% Fe₃O₄ Nps/10% N- Nicotinyln-N', N''-bis (Hexamethylenyl) phosphoric triamide (HE) was designed, fabricated, and fully characterized. The devised nanocomposite was applied to remove Cd(II) ions from two kinds of contaminated water samples, namely an aqueous solution of Cd(II) ions and an industrial wastewater sample obtained from the Narin metal-plating factory with a pH=9 and an unknown complex structure. The results revealed that the percentage of the Cd (II) ions removed by the prepared nanocomposite was not only acceptable, but it was also high. This rate, both for the aqueous solution (99.9%) and the real industrial wastewater sample (99.5%), was even higher than those reported for other similar nanocomposites.

Acknowledgments

The support of this work by the Iranian Research Organization for Science and Technology (IROST) is gratefully acknowledged.

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